CHESAPEAKE BAY WATER-QUALITY MONITORING PROGRAM

RIVER INPUT NUTRIENT AND SEDIMENT LOADING TRENDS COMPONENT

QUALITY ASSURANCE PROJECT PLAN

JULY 1, 2003 to JUNE 30, 2004

MARYLAND DEPARTMENT OF NATURAL RESOURCES RESOURCE ASSESSMENT SERVICE

IN COOPERATION WITH THE U.S. GEOLOGICAL SURVEY

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Quality Assurance Project Plan

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A. Project Management

A.1 Introduction

This Quality-Assurance Project Plan (QAPP) describes quality-assurance goals and measures for the River Input monitoring program designed to support Chesapeake Bay restoration programs.

The project, the *Chesapeake Bay River Input Monitoring Program*, includes the monitoring of nutrient and suspended-sediment concentrations and streamflow in selected Maryland rivers representing major inflow to Chesapeake Bay. This project is supported through Maryland's Department of Natural Resources (MD DNR) and U.S. Geological Survey (USGS) cooperative funds. The objectives of this project are to:

- characterize present flows and pollutant loads to the Bay and its tributaries;
- determine trends that might develop in response to pollution-control programs in the Bay's major watersheds; and
- integrate the information collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting the water quality of the Chesapeake Bay.

The MD DNR and the USGS conduct this project cooperatively. Sampling events, goals, and objectives for this project are overseen by the USGS project manager, Michael P. Senus.

A.2 Distribution List

This QAPP will be distributed to the following project participants:

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A.3 Project/Task Organization

J. Shermer Garrison, MD DNR, Tidewater Ecosystem Assessment, serves as the Project Coordinator for the Maryland River Input project. He is tasked with assuring that all project commitments, the project timetable, and deliverables are completed.

Michael P. Senus, USGS, is the Project Manager for the River Input Monitoring Program and is responsible for coordinating Nutrient Trend Loading sampling programs in PA, MD, and VA, coordinating and evaluating data, quality assurance and quality control for the program, and producing USGS reports.

Bruce Michael is MD DNR's Chesapeake Bay Program Grants Coordinator. He is tasked with reviewing quality-assurance reports on these projects.

Cherie V. Miller is the USGS District Water-Quality Specialist. As a quality assurance officer she is tasked with conducting field audits, and reviewing reports. While these are regular responsibilities of the

USGS District Water-Quality Specialist and she may recommend additional quality-control activities to the USGS Project Officer if necessary. Her responsibilities are generally limited to activities in the MD-DE-DC District office, and she may request assistance from Water-Quality Specialists in the Virginia and Pennsylvania Districts for activities in those offices.

A.4 Problem Definition/Background

The decline in water quality of the Chesapeake Bay within the last decade has, in large part, been attributed to excessive nutrients entering the estuary from its surrounding tributaries. In an effort to improve the water quality of the Bay, Federal, State, and local governments have initiated point and non-point source nutrient-reduction programs within the tributary basins discharging to the Bay. Monitoring at key sites can help to quantify improvements in water quality and verify the effectiveness of nutrient-control measures implemented in the watersheds.

In addition, the quality of the river discharge, and the timing and magnitude of the pollutant concentrations and loads delivered to the estuary are important data needed to enhance knowledge of or need to strengthen other components of the Chesapeake Bay water-quality monitoring program. The integration of all of these components will lead to a better understanding of the factors influencing water quality that can then be translated into better water-quality management for the Bay and its tributaries.

With these general goals in mind, the Maryland Department of Natural Resources' (MD DNR) Resource Assessment Service, in cooperation with the USGS, initiated the River Input Monitoring component of the Chesapeake Bay Water-Quality Monitoring Program.

Four major tributaries – the Susquehanna, Potomac, Patuxent, and Choptank Rivers – were initially selected for monitoring in 1985 by the State of Maryland. Combined, these rivers contribute over 70 percent of the flow to the entire Chesapeake Bay and they contribute nutrients and sediments from a wide range of land-use, geologic, and hydrologic conditions found in the Bay watershed. A monitoring program was established near the most downstream non-tidally affected part of each river to monitor nutrient and sediment concentrations and streamflow to help calculate transport of these nutrient and sediment loads to tidal tributaries of the Bay.

A.5 Project/Task Description

Water-quality samples that are representative of the entire river cross section are collected and later analyzed to determine concentrations of selected nutrient species and suspended sediment in the river. These samples are collected during different seasons across different flow regimes. When combined with the continuous, 15-minute flow record from the USGS gage at each station, it is possible to estimate nutrient and sediment loads on a monthly and annual basis with a known level of confidence. Additionally, water-quality field measurements are made for dissolved oxygen, pH, alkalinity, specific conductance, water temperature and air temperature.

The USGS's National Field Manual for the Collection of Water-Quality Data (Wilde and others, 1998, http://water.usgs.gov/public/owq/FieldManual/index.html) describes the sampling process in detail. Data-collection quality will be monitored by the assessment of field blanks and replicates and by annually conducting and documenting the results of random field audits.

Sampling will be performed during each season. Field data will be entered and quality-assured monthly. Streamflow, nutrient, and suspended-sediment concentration data sets from each monitoring station will be forwarded to J. Shermer Garrison at MD DNR by March 31 of each year. A final data set with mean monthly and annual loads of nutrients and suspended sediment will be forwarded to J. Shermer Garrison by October 15 of each year. Quarterly reports describing field activities, quality-control results, and data-management issues will be submitted with the data to J. Shermer Garrison. Additionally, data interpretation of nutrient trends and trend explanation will be performed by project hydrologists and incorporated into various USGS and/or MD DNR reports.

A.6 Data-Quality Objectives and Criteria for Measurement Data

This study provides Chesapeake Bay resource managers with information that can help to quantify changes in water quality, quantify nutrient loads critical for evaluating progress towards reducing controllable nutrients to the Bay, and verify the effectiveness of nutrient-control measures taken in the watersheds. A calibrated model that can simulate: constituent relationships, seasonal variation, and changes in trends was developed. As a result, relatively few water-quality samples need to be collected throughout the year under different streamflow conditions to determine loads within a known confidence interval. Once completed, this information is then given to researchers and Bay resource managers.

A.7 Special Training Certification

Field personnel must be trained in water-quality sampling operations, record management, quality-assurance procedures, vehicle operations, and maintenance and troubleshooting. Laboratory personnel must by trained in analytical methods, quality-control procedures, record management, maintenance and troubleshooting.

A.8 Documentation and Records

Water-quality field measurements of temperature, dissolved oxygen, pH, alkalinity, and specific conductance are recorded at each site. Additionally, water-quality samples are collected and submitted for analysis to the USGS National Water-Quality Laboratory in Denver, Colorado. Samples are evaluated for total and dissolved Kjeldahl nitrogen (ammonium plus organic nitrogen), dissolved nitrite, dissolved nitrate plus nitrite, dissolved ammonia, total and dissolved phosphorus, dissolved orthophosphate, dissolved silica and total organic carbon. Suspended sediments are analyzed at the USGS Sediment Laboratory in Louisville, Kentucky.

All data will be recorded using standardized data sheets for the specific projects (Attachment A). These data will be keyed into the USGS data management systems by technicians who collect the data. These data will be provided to MD DNR in hard copy in the form of tables and data summaries that will be included in reports. Electronic data will be submitted with the final deliverables in ASCII text files via diskette or File Transfer Protocol (FTP) via the Internet.

Additionally, a web site has been created to provide detailed information about the project as well as simple access Maryland's concentration and load data. The site includes general information, data retrieval options, a water chemistry page that describes sources and chemical behavior of the water-quality constituents, trends in the constituents, methods used in the project, Chesapeake Bay related publications and links, a glossary, and a bibliography. This site can be accessed at: http://www-va.usgs.gov/chesbay/RIMP/.

B. Measurement/Data Acquisition

B.1 Experimental Design

This document provides a detailed description of the monitoring and analysis components of a study conducted by the MD DNR Assessment Service, in cooperation with the USGS, to quantify nutrient and suspended-sediment loads entering the Chesapeake Bay from a number of tributaries to the Bay and to determine trends in constituent-concentration data occurring at these tributary stations.

The number of events to be sampled and the number of samples per event is based on the requirements of the load-computation model. A long-term sampling record at the four River Input sites (Susquehanna, Potomac, Patuxent, and Choptank Rivers) has allowed for the development of a modeling process that permits fewer samples to be taken in order to characterize nutrient and sediment loads. Water-quality samples need to be collected during each season during base flow and under various stormflow conditions. "Continuous" flow measurements also need to be collected. Using a multivariate model, the seasonal relationship between constituent concentration and streamflow at each site is established. Using the continuous flow record, a cumulative load of nutrients and sediment can be determined.

Station Description

The location of monitoring stations were chosen by determining the location of existing stream-gaging stations near the lowest nontidal reach of each selected rivers. The monitoring stations selected are in the Susquehanna River, Patuxent River, Choptank River, and the Potomac River in Washington D.C.. The location of the monitoring sites and drainage area information are presented in table 1.

Table 1. Location of River Input Monitoring site	fable 1.	Location	of River	Input N	Monitor	ing site
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Program	Station Name	USGS Station	Bay Program Station	Latitude deg-min-sec	Longitude deg-min-sec	Drainage (sq. mi.)
		Station	Station	ueg-IIIII-3ec	ueg-IIIII-sec	(34. 1111.)
River Input	Susquehanna River at	01578310	CB1.0	39-39-28	76-10-29	27,100
River Input	Conowingo, MD Potomac at Chain	01646580		38-55-46	77-07-02	11,570
River Input	Bridge River, D.C. Patuxent River nr.	01594440	Near TF1.0	38-57-21	76-41-36	348
River Input	Bowie, MD Choptank River nr.	01491000	ET5.0	38-59-50	75-47-10	113
	Greensboro, MD					

B.2 Sampling Method

Except for the Potomac River at Chain Bridge site, USGS personnel collect all water samples at each River Input monitoring station in accordance with the USGS National Field Manual for the Collection of Water Quality Data (Wilde and others, 1998). Samples for nutrient and suspended-sediment analysis are collected at each river. The Occoquan Watershed Monitoring Laboratory (OWML), working for the Metropolitan Washington Council of Governments (MWCOG) under contract to MD DNR, collects baseflow and stormflow water-quality samples from the Potomac River at Chain Bridge (01646580) and provides the discrete stormflow sampling data to USGS (Department of Environmental Programs, 1987). The Metropolitan Washington Council of Governments and USGS coordinate this data transfer. Base-flow water-quality data are collected at fixed intervals on a monthly basis at the Potomac River station as part of the USGS National Water-Quality Assessment (NAWQA) program.

Base-flow samples are collected at least monthly and stormflow samples are collected seasonally, with an average coverage of three storms per season. The monitoring program emphasizes the collection of water-quality samples during periods of high flow (storm-event sampling), because most of the river-borne nutrient and suspended-sediment load is associated with storm events. Discrete samples are collected during storm events along the rise, peak, and fall of the hydrograph. Water-discharge data are also collected for each of the rivers throughout the period.

In the USGS program, flood stage events are predicted through weather forecasts and by remote monitoring of river stage from the USGS offices. In the MWCOG sampling program, storm-event sampling is initiated automatically by an increase in the river stage at the USGS gage located upstream of Chain Bridge, at Little Falls, Maryland (01646500).

Water-quality samples are collected using a stainless-steel weighted bottle sampler. This weighted bottle sampler holds up to a 1-liter bottle made of either Teflon or polyethylene or glass. The sampler is lowered to the water by using a hand reel and synthetic rope (nylon or polyethylene) configuration. The general approach used to collect water samples is the Equal-Width Increment (EWI) sampling method, with minor variations to conform to site conditions. Such samples are typically depth-integrated using a transit-rate technique and small-neck bottle. There is an eight-inch unsampled zone due to the distance from the channel bottom to the sample bottle neck's opening. In the case of the Potomac River at Chain Bridge, where depth-integrated samples cannot be collected because of flow conditions, previous testing has shown that the water column at this location is well-mixed and samples within the near surface zone (1-2 meters) are considered to be representative. Similarly, restricted access on the Susquehanna River at Conowingo Dam requires that a variation of Equal-Discharge Increment (EDI) sampling be used. Previous testing at Conowingo Dam has shown that this approach provides a representative sample for flows confined to the turbines. However, sampling from the turbines can be unrepresentative of spillway discharges since the flows originate from different locations in the reservoir's vertical profile. Sampling from the spillway during high flows is currently not allowed because of safety concerns.

Susquehanna River

USGS personnel collect water samples from the Susquehanna River at Conowingo Dam in Conowingo, Maryland. Base-flow and stormflow samples are collected using the equal discharge increment method. This method involves the collection of water-quality samples at the centroids of equal discharge increments along the turbine outflow. Water samples are collected using a stainless-steel weighted bottle sampler suspended from the catwalks at the turbine outflow. The number and location of cross-section samples are dependent on the characterization of flow from the turbines at the time of sampling.

Storms on the Susquehanna, for the purpose of this QAPP, are operationally defined as occurring when water passes over the spillway. This represents a storm discharge exceeding 80,000 cubic feet per second (ft^3/s), the maximum turbine capacity.

Potomac River

Potomac River storm water samples will be collected by Occoquan Watershed Monitoring Laboratory (OWML) personnel using an automatic sampler located at Chain Bridge, in Washington D.C from July 1, 2003 through December 31, 2003. The sampler is programmed to draw regular frequency samples as well as discrete daily samples during high-flow events. High-flow events are defined by the river stage exceeding a designated value. Once this occurs, the sampler draws samples once daily for the duration of

the event. There is no direct coordination between the Occoquan Laboratory and the USGS on regular sampling activities.

USGS personnel collect monthly baseflow samples at Chain Bridge in Washington, D.C. using the EWI method. This method involves the collection of water-quality samples at the centroids of equal width increments along the river cross section. Water-quality samples are collected using a stainless-steel weighted bottle sampler. The number and location of cross-section samples are dependent on the characterization of flow at the time of sampling. During most flow conditions, samples are collected from five points along the river cross section.

Beginning January 1, 2004, USGS will pick up storm sampling from OWML. An automatic sampler will not be used. Instead, the USGS will collect samples manually. Cross-sectional, depth-integrated water-quality samples will be collected manually during stormflow conditions at five sections along Chain Bridge. Isokinetic samplers such as the D-95 are not an appropriate method of sampling off Chain Bridge due to lack of a sampling platform as a result of high volumes of traffic on Chain Bridge. Therefore, these samples will be collected using a stainless-steel weighted bottle sampler with a 0.5-liter Teflon bottle suspended by a polyethylene rope.

A storm event on the Potomac River at Chain Bridge is operationally defined as a USGS gage height at Little Falls of greater than 5.0-ft or a discharge of greater than 20,000 cubic feet per second (cfs or ft³/s). A storm (or high-flow) event is a significant increase in discharge based on the antecedent precipitation, the magnitude of discharge, and the season of the year. Storms selected are dependent on the previous sampling history. An attempt is made to sample a representative range of storm types and sizes throughout the year.

Patuxent River

USGS personnel collect Patuxent River water samples at Governors Bridge on Governors Bridge Road in Bowie, Maryland. Cross-sectional, depth-integrated water-quality samples are collected manually during base-flow and stormflow conditions at five sections along the bridge. Base-flow samples are collected using a stainless-steel weighted bottle sampler with a 0.5-liter Teflon bottle suspended by a polyethylene rope. Stormflow samples are collected using a DH-59, DH-95, or D-95 depth-integrated isokinetic sampler. When possible, stormflow samples are collected throughout the rise, peak, and fall of the storm hydrograph for selected storm events.

A storm event on the Patuxent River at Bowie is operationally defined as a USGS gage height of greater than 7.5-ft or a discharge of greater than 800 cubic feet per second (cfs or ft³/s). A storm (or high-flow) event is a significant increase in discharge based on the antecedent precipitation, the magnitude of discharge, and the season of the year. Storms selected are dependent on the previous sampling history. An attempt is made to sample a representative range of storm types and sizes throughout the year.

Choptank River

USGS personnel collect Choptank River water samples at Christian Park located at the end of Red Bridges Road in Greensboro, Maryland. Prior to the spring of 2000, an abandoned automobile bridge across the river served as the sampling platform. For safety reasons, the bridge was removed by the Caroline County Department of Public Works. The bridge was replaced as a sampling platform in fall

2001 by a cableway system constructed by the USGS. The cableway with A-frame anchors is a standard USGS river crossing system that is often used to sample inaccessible rivers.

Cross-sectional, depth-integrated samples are collected during base-flow and stormflow conditions at five to ten points across the stream channel. Baseflow and stormflow samples are collected using a 1-liter stainless-steel weighted bottle sampler.

During low-flow (including both base-flow and lower stormflow) conditions, samples are collected by wading across the stream channel. During higher stormflow, the cableway system is utilized.

During high-flow (storm) events, conditions sampling is performed with a 35-pound DH-95 or a 65-pound D-95 (both samplers are composed of an aluminum body with Teflon fins) operated from a cablecar that traverses along the cableway.

A storm event on the Choptankt River near Greensboro is operationally defined as a USGS gage height of greater than 4.0-ft or a discharge of greater than 400 cubic feet per second (cfs or ft³/s). A storm (or high-flow) event is a significant increase in discharge based on the antecedent precipitation, the magnitude of discharge, and the season of the year. Storms are selected for sampling depending on the previous sampling history. An attempt is made to sample a representative range of storm types and sizes throughout the year.

Storm samples can also be collected remotely via a modem-activated, automated point sampler. This autosampler is located on the eastern bank of the Choptank River inside the USGS gage house. The sampler's intake is located 10 feet from the water's edge of the left bank, anchored 3 inches above the streambed. The autosampler was calibrated by comparisons made against manually collected samples shortly after its installation (September 2000 and July 2002).

Constituents Monitored

The monitoring program focuses on quantifying the water quality and loads of major nutrient species and suspended sediment from the nontidal parts of the Susquehanna, Potomac, Patuxent, and Choptank Rivers. Chemical parameters monitored for the program include:

TKN total Kjeldahl nitrogen

DKN dissolved Kjeldahl nitrogen

TDN total dissolved nitrogen

TPN total particulate phohsphorus

NO2 dissolved nitrite

NH4 dissolved ammonia as N

NO23 dissolved nitrate plus nitrite as N

TP total phosphorus

PP particulate phosphorus

PIP particulate inorganic phosphorus

TDP total dissolved phosphorus

o-PO4 dissolved orthophosphorus as P

SiO2 dissolved silica

TOC total organic carbon

DOC dissolved organic carbon

PC particulate carbon

particulate inorganic carbon

PIC TSS total suspended sediment

SSC total suspended solids

chlr a chlorophyll-a and pheophytin

Analytical methods for these constituents are shown in table 2.

B.3 Sample Handling and Custody

Sample Treatment and Preservation

Water-quality samples collected by the USGS (Wilde and others, 1998) are split using either a polypropylene churn splitter or, if samples were simultaneously collected for pesticide analysis, using a fluorocarbon polymer (Teflon) cone splitter (Wilde and others, 1998). When the churn splitter is used, the composite sample is introduced into a pre-cleaned plastic churn splitter and sub-samples for whole-water analysis are drawn while churning at a rate of 1.0 ft/second. The remaining samples are filtered on site for dissolved analysis using a 0.45-micrometer (average pore size, polycarbonate) capsule filter (Wilde and others, 1998). When the cone splitter is used, whole-water samples are split from the entire sample into their respective bottles using a pre-cleaned cone splitter and the remaining sample is filtered on site for dissolved analysis using a 0.45-micrometer capsule filter. After acid is added to the appropriate samples for preservation, the nutrient samples are placed immediately on ice and chilled to a temperature of 4 degrees Celsius. Suspended-sediment samples, collected concurrently with the water-quality samples from the churn splitter or collected separately, are shipped to the USGS Sediment Laboratory in Louisville, Kentucky, for analysis. Chain-of-custody procedures follow recommended USGS National Water-Quality Laboratory procedures.

Table 2. River Input Monitoring sampling parameters.

Parameter Code	Parameter/ Methodology	Reference	Reporting Level
P00623	Dissolved Kjeldahl Nitrogen (DKN) (Ammonia plus Organic Nitrogen, TKNF) <i>Block Digest, Colorimetry</i>	Fishman and Friedman (1989)	0.1000 mg/L
P00625	Total Kjeldahl Nitrogen (TKN) Block Digest, Colorimetry 1-4552-78	Fishman and Friedman (1989)	0.1000 mg/L
P49570	Particulate Nitrogen (PN) Elemental Analysis on filter	EPA method 440.0	0.0220 mg/L
P62854	Total Dissolved Nitrogen (TDN) Alkaline Persulfate N (filtrate)	Fishman and Friedman (1989)	0.0300 mg/L
P00613	Dissolved Nitrite as Nitrogen (NO₂) Colorimetry, Diazotization 1-2540-78	Fishman and Friedman (1989)	0.0100 mg/L
P00631	Dissolved Nitrite & Nitrate as NO ₂₊₃ Colorimetry, Cd-reduction Fishman and Friedman (1989)		0.0500 mg/L
P00608	Dissolved Ammonia (NH₃) Colorimetry, Auto 1-2522-78	Fishman and Friedman (1989)	0.0200 mg/L
P00665	Total Phosphorus (TP) <i>Block Digest, Colorimetry</i> I4600-81	Fishman and Friedman (1989)	0.0080 mg/L
P00666	Total Dissolved Phosphorus (TDP) Acid Persulfate (filtered)	EPA method 365.1	0.0044 mg/L
P00666	Total Dissolved Phosphorus (TDP) Alkaline Persulfate (filtered)	Fishman and Friedman (1989)	0.0100 mg/L
P00671	Dissolved Orthophosphate (DIP or o-PO ₄) Colorimetry, Auto I-2601-81	Fishman and Friedman (1989)	0.0100 mg/L
P00995	Dissolved Silica (Si) Colorimetry, Auto 1-2700-78	Fishman and Friedman (1989)	0.1000 mg/L Si02
P00680	Total Organic Carbon (TOC) Wet Oxidation 0-3100-83	Wershaw and others (1987)	0.2700 mg/L
P80154	Total Suspended Sediment (SSC) Hydroscopic glass-fiber filtration ASTM test method D3977-97 Method C	Sholar and Shreve (1998)	0.5000 mg/L

B.4 Analytical Methods

Analytical Methods employed Analytical methods for these constituents are documented in table 2 and described in the USGS National Water-Quality Laboratory documents.

Laboratory Analysis

Water-quality samples collected by the USGS for the River Input Monitoring Program are analyzed by the USGS National Water-Quality Laboratory (NWQL) in Denver, CO, Chesapeake Biological Laborotory (CBL) in Solomns, MD, and Department of Health and Mental Hygiene (DHMH) in Baltimore, MD. Analytical techniques employed by the laboratory are documented in table 2. Sediment samples are analyzed by the USGS Sediment Laboratory in Louisville, Kentucky (Sholar and Shreve, 1998).

B.5 Quality Assurance/Quality Control

Quality assurance and quality control are a significant component of the monitoring program. The quality-assurance effort includes documentation of concentration variability within the cross section, sediment-transport analysis, quality assurance of sample-collection techniques and field personnel, and accounting for variability within and among the analyzing laboratories. Quality-assurance results can be obtained from: USGS, Water Resources Division, MD-DE-DC District office, at 8987 Yellow Brick Road, Baltimore, MD, 21237.

Laboratory quality-control methods are documented in the USGS National Water-Quality Laboratory (NWQL) Quality Control manual (Pritt and Raese, 1995; also available at http://wwwnwql.cr.usgs.gov/Public/pubs/QC Fact/text.html).

Field quality control is checked during random field audits. The Quality Assurance officer assures that samples were collected, labeled, and preserved according to standard operating procedures. A field checklist will be prepared, and a summary report will be submitted.

Field blanks are submitted to evaluate field accuracy and handling of samples. Split samples are collected semi-annually (in December and June) and submitted to the USGS's National Water-Quality-Laboratory in Denver, Colorado, the Maryland Department of Health and Mental Hygiene (DHMH) Laboratories Administration in Baltimore, Maryland, the University of Maryland's Chesapeake Biological Laboratory in Solomons, Maryland and the Occoquan Watershed Monitoring Laboratory (OWML) in Occoquan, Virginia. Results are forwarded to MD DNR and USEPA.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance

Instrument probes are cleaned and thoroughly inspected between sampling events. If any probe is not functioning correctly, it is determined whether it is necessary to perform maintenance and/or replace (retire) the instrument.

Physical sampling gear is inspected before each use to assure that all parts are intact. Any gear that shows operational deficiency is not used until repairs can be made.

B.7 Instrument Calibration and Frequency

The meters used to determine field parameters are calibrated daily. Specific instructions for calibration are found in the operating manuals provided with the instrument. Fresh standards are available for calibration prior to each sampling period. The field technician is responsible for providing directions for appropriate calibration, including the appropriate potassium chloride concentration to use for salinity calibrations. Dissolved oxygen (DO) is measured using either a Winkler Titration kit or YSI DO meter. The DO meter is calibrated using the saturated air method.

A calibration record is maintained for each unit in a log book. This log serves as documentation for preand post-calibration information for each parameter recorded. The log is useful in determining drift in a probe, which indicates that maintenance is necessary for maintenance. The field technician remains aware of questionable performance of any instruments, and determines when it is necessary to perform maintenance and/or replace an instrument.

B.8 Inspection Acceptance Requirements for Supplies and Consumables

The field technician routinely inspects equipment and supplies. The field technician is responsible for determining when supplies and consumables should be discarded. Special attention should be paid to the condition of any filtration supplies (pads, bottles, etc.) and ultra-clean gear to assure that they are uncontaminated. If contamination is suspected, the supplies should be discarded. Any supplies that have exceeded their expiration date are disposed of.

B.9 Data Acquisition

All data will be collected using standardized data sheets for the specific projects. These data will be keyed into the USGS's data management systems by technicians who collect the data. All data files will be documented in metadata files. Data files will be maintained on the USGS computer network and backed up by diskette and raw datasheets. The USGS MD-DE-DC District office in Baltimore will house the archived copies. Copies of the original data sets will be provided to MD DNR and maintained by the project coordinator. Electronic files with appropriate metadata will be forwarded to the appropriate analysts. The project data manager will maintain field data sheets, which will be kept at the same location as the electronic files.

B.10 Data Management

All data collected will be entered on field data sheets designed for each study (see Attachment A). Data sheets will be coded with a site code (sample area and station number, date, collection time, and collector's initials). Data sheets will be gathered at the end of the day and placed in a notebook. Originals of all data sheets are maintained in the USGS MD-DE-DC District library and may be sent to the USGS National Archives at a later date.

The field technician or senior field staff person will verify all data entered in the field. This person will examine all data sheets to ensure that they are accurately and legibly completed. They will then sign and record the date and time on the data sheets when verified. All field validation must occur prior to leaving the site before samples are discarded. Any recording errors are to be marked through and initialed. The true value is to be recorded next to the error, and all errors are to be explained in the remarks column of the data sheet.

Field data are entered into the USGS computers using standard USGS data entry procedures. Summary statistics are calculated to identify anomalies in the data. All data anomalies are verified against the raw

data and corrected if necessary. Several times during the year, some provisional data files will be transferred from USGS to MD DNR via diskette or file transfer protocol via the Internet. These intermediate data transfers include flow data from each station for the previous calendar year, raw nutrient and suspended-sediment data and quality-control results from the previous calendar year, and draft and final daily and monthly load estimates for each nutrient and suspended-sediment parameter monitored during the previous calendar year. Metadata files created by the data manager and linked to the data files also will be transferred to MD DNR.

B.11 Data Analysis

Data analysis for load estimation is performed by USGS project staff from the Maryland, Virginia, and Pennsylvania District offices, and by staff from the Susquehanna River Basin Commission (SRBC).

Although a simple linear model can adequately describe a streamflow-parameter concentration relation for some nutrient or sediment constituents, such a model will not work for all constituents. A single model that can simulate the variable streamflow-concentration relations in different watersheds and other issues would be helpful. Past experience has shown that the quadratic flow parameter was significant for many monitored constituents, which indicates that the relation of concentration to water discharge for these constituents requires a more complex model. For some constituents, seasonal variability in concentration occurs, and a single model should be able to account for seasonality. Finally, a sufficiently long record can help determine trends or changes in concentration over time, but when a data record is long enough, for some constituents changes in trends (acceleration or deceleration in trend) may occur and a model needs to be able to determine changes in trends.

Load-Estimation Procedure

Load estimates were calculated using multi-variate linear regression. Monthly and annual mean-daily loads were calculated for each river for total phosphorus (TP), dissolved phosphorus (TDP), dissolved orthophosphorus (PO₄), total nitrogen (TN), total Kjeldahl nitrogen (TKNW), filtered Kjeldahl nitrogen (TKNF or FKN), dissolved Nitrite (NO₂), dissolved nitrite plus nitrate (NO₂+ NO₃), dissolved ammonia nitrogen (NH₄), total organic carbon (TOC), dissolved silica (SI), and total suspended sediment (SSC).

The model used in determining nutrient and suspended-sediment loads entering the Chesapeake Bay from the River Input stations is estimated using the minimum variance unbiased estimator (MVUE) of Bradu and Mundlak (1970) which employs a 7-parameter log-linear model (Cohn and others, 1989; Gilroy and others, 1990). Monthly and annual loads and corresponding confidence intervals are determined and reported annually.

The load-estimation procedure involves two steps. First, a linear model is fit by ordinary least squares (Draper and Smith, 1981) to the logarithms of the concentration and flow data:

$$\ln[C] = \boldsymbol{b}_0 + \boldsymbol{b}_1 \bullet \ln[Q/\overline{Q}] + \boldsymbol{b}_2 \bullet \left\{ \ln[Q/\overline{Q}] \right\}^2 + \boldsymbol{b}_3 \bullet \left[T - \overline{T}\right] + \boldsymbol{b}_4 \bullet \left[T/\overline{T}\right]^2 + \boldsymbol{b}_5 \bullet \sin[2\boldsymbol{p} \bullet T] + \boldsymbol{b}_6 \bullet \cos[2\boldsymbol{p} \bullet T] + \boldsymbol{e}$$
(1)

where

ln [] = natural logarithm function,

C = constituent concentration in milligrams per liter (mg/L),

b's = parameters estimated by ordinary least squares,

Q = water discharge in cubic feet per second (ft^3/s) ,

T = time measured in years,

sin = sine function,

cos = cosine function, and

e = independent, random error.

The above MVUE model (1) requires estimation of 7 parameters: b_0 is a constant; b_1 and b_2 describe the relation between concentration and discharge; b_3 and b_4 describe trends in concentration data; and b_5 and b_6 describe seasonal variability in concentration data. The errors, denoted e, are assumed to be independent, and normally distributed with zero mean and variance s^2_{e} . Q and T are "centering" variables that improve the numerical precision of the estimates (Draper and Smith, 1981). Q and T are defined so that b_1 and b_2 , and b_3 and b_4 , respectively, are not correlated.

Next, daily load estimates are computed using the MVUE, and added together to provide monthly and annual mean-daily load estimates. The standard errors of these estimates are computed using formulas discussed in Gilroy and others (1990) and Cohn and others (1992). Approximate confidence intervals were computed by subtracting and adding two standard errors from the estimated mean load.

Statistical aspects of the MVUE are discussed in Cohn and others (1989) and Gilroy and others (1990). Practical aspects are described in a technical memorandum (Cohn and others, 1992b), which provides an example of its application. The FORTRAN program ESTIMATOR_92, which implements the MVUE, was employed for this project. The program is documented in Baier and others (1992).

The validity of the MVUE was investigated by Cohn et al. (1992), using monitoring data collected for this study. The MVUE performed well even though some model assumptions, such as independent and normally distributed errors, were violated to some extent. These results, in combination with the examination of residual plots and other model diagnostics, lend support to this application of the MVUE.

The load-estimation procedure described above is desirable for several reasons. The model is sufficiently flexible to capture many of the characteristics of real constituent data; it is easy to use--ordinary least squares is a particularly easy method for fitting data; statistical properties of the estimates are well understood; it employs only seven parameters to describe discharge, seasonality, and time trends; and it has generally been found to "explain" between 10 and 80 percent of the variability observed in the logarithms of constituent concentration data.

Calibration Data

For each year, the load-estimation model is calibrated using the data set collected and analyzed by the USGS from that site for the previous 9 years. For the Susquehanna, Potomac, Patuxent and Choptank Rivers, a constant 9-year window is used, with the middle year considered the best and "final" load estimate and the final four loading years considered "provisional".

Seasonal Variability and Long-Term Trends in Constituent Concentration Data

Model results and regression summaries are used to characterize the relation of constituent concentration to river discharge and season, and to determine if concentration has changed over time. Model results and regression summaries are documented and parameter coefficients (β 's) are tabulated for each constituent. Statistically significant parameters are identified; a (+) sign indicates positive parameter coefficients and a

(-) sign indicates negative parameter coefficients. Regression statistics, R^2 (standard error) are determined and included in the summaries.

Interpretations of model results are based on the significance and sign (+/–) of model parameters. Model parameters are considered significant if the regression statistic "p value" is greater than 0.05 and the absolute value of the "T statistic" is greater than 2.0. Significance of the model parameter indicates a relation between constituent concentration and the corresponding model variable (discharge, time, or season). The sign of a model parameter indicates whether it has a positive (+) relation to the concentration or a negative (–) relation.

The relation between constituent concentration and discharge is defined in the model form (1) by both a linear $(\ln[Q/\overline{Q}])$ and a quadratic-flow variable $(\ln[Q/\overline{Q}]^2)$. A significant linear parameter indicates a linear relation between concentration and discharge. A significant quadratic parameter indicates a nonlinear relation between concentration and discharge. If both the linear and quadratic-flow parameters were significant, an acceleration (+) or deceleration (–) in constituent concentration occurred. For example, a significant positive linear-flow parameter combined with a significant negative quadratic-flow parameter indicated that concentration would increase with increasing flow, but the rate of increase in concentration would decelerate, or decline, at higher flows.

The relation between constituent concentration and time is represented by both a linear $\left(T-\overline{T}\right)$ and quadratic-term variable $\left(T-\overline{T}\right)^2$ in the model form. A significant linear parameter indicates an upward (+) or downward (-) linear trend in constituent concentration. A significant quadratic parameter indicates a non-linear relation between concentration and time. For example, a significant, positive quadratic parameter indicates a decreasing trend in early years followed by an increasing trend in later years. A significant, negative quadratic parameter indicates the opposite. If both the linear and quadratic-time trend parameters were significant, then an acceleration (+) or deceleration (-) in trend occurred in later years.

Seasonality was defined in the model form by two variables, $\sin(2p \bullet T)$ and $\cos(2p \bullet T)$. If one or both of the seasonality variables were significant, seasonality was considered an important factor in describing the variability in constituent concentration at the four river stations.

Estimates of Loads

The same model form (1) is used to estimate monthly and annual mean-daily loads for each constituent at each of the monitoring stations. Although all parameters are included in each of the model runs, not all parameters are significant. The presence or absence of a non-significant parameter does not affect the value of the resulting load estimate. However, inclusion of non-significant parameters does result in slightly larger standard errors of the estimate, which causes an over-estimation of confidence limits for the estimates. As this results in a slight understatement of the accuracy of the estimates, using all seven parameters in the model provides for a conservative assumption.

Residuals are reviewed for determining whether serious violations of the assumption of normality occur and that all of the models reasonably represent the data. The statistical significance of each model equation is determined.

Monthly and annual mean-daily load estimates for the following constituents are calculated for the River Input sites: TP, TDP, PO4, TN, TKNW, TKNF or FKN, NO₂, NO₂+ NO₃, NH₄, TOC, SI, and SSC. Error terms also are calculated. Monthly load estimates can be calculated by multiplying the mean-daily load by the number of days in a given month. Annual loads can be calculated by multiplying the mean-daily load by 365 days.

It is understood that the relation between concentration and streamflow may change over time due to changes in land use, wastewater discharges, best management practices and climate change, so a moving window approach was developed to estimate loads. For some parameters in the four Maryland rivers, differences were observed for loads estimated using a 14-year (1985-1998) and a 10-year (1989-1998) model window, especially those near the tail of the calibration period. Estimates near the center of a model window (Year-5 of a desired 9-year window) have the least uncertainty. Load estimates in the first and last 4-year period are considered preliminary and are revised each year. So, for each year, a new model is run for each site and constituent, the most recent year of data are added to the data set and the previous 4 years of estimates are updated. The fifth (middle) year of data is considered to be the best estimate and is kept in the final database. This revised methodology provides a greater confidence in load estimation (Yochum, 2000).

C. Assessment/Oversight

C.1 Assessment and Response Actions

The quality-assurance officer will conduct random field and office audits to ensure that data collection and data manipulation follow guidelines set forth in the to the quality-assurance plan. A minimum of one field audit will be conducted each year. The field audit will consist of examining all aspects of the field collection for accuracy and adherence to sampling procedures. The field audit will be representative of all sites, but will not necessarily require a visit to each site. A summary report documenting the field activities will be provided. Office audits will be conducted to ensure that all logs are completed and up-to-date, and that proper data management and manipulation is being conducted. The principal investigator will be immediately notified of any deficiencies and take immediate corrective actions.

The project coordinator will continually monitor the logs and records associated with the project to assure that project schedules are being met. The project coordinator will immediately take any corrective action necessary if project schedules and procedures are being violated. The quality-assurance officer will perform and report on technical system audits and data-quality audits. Peer review of the project design and results will be solicited. Experts in the various field of study will be contacted for comments and suggestions on data analysis and study elements. Data-quality assessments will be conducted to determine whether the assumptions were met.

C.2 Reports to Management

Quarterly progress reports will be submitted from the USGS to MD DNR to describe quarterly project activities (Attachment B). Any deviations from scheduled project activities will be noted and the effect of these deviations on the final project outcome will be described. Corrective measures will also be suggested. The River Input Project Manager (USGS) will be responsible for producing and distributing progress reports.

D. Data Validation and Usability

D.1 Data Review, Validation, and Verification

Data will be verified using a previously developed data quality-control system. After being scrutinized during the data-entry phase, data are analyzed and plotted to examine any outliers or anomalies. These are then examined, verified, and corrected if necessary. Field audits are performed to assure that all data are collected according to standard operating procedures, and that the collection effort is consistent and equal. The USGS Project Manager is responsible for performing quality control, or assuring that quality control is performed by appropriate staff.

All field logs and information will be thoroughly reviewed prior to data analysis to assure that all data were collected uniformly. Any data that were not collected according to standard operating procedures will be examined to determine whether they are representative. All quality-assurance reports will be examined prior to data analysis to verify that data were properly and consistently collected. Any deviations in data collection will be taken into account during data analysis. All calibration logs will be examined to determine how well the measurement instruments performed. If there appears to be significant drift in instrument performance, the data will be adjusted accordingly. All raw data will be kept in paper files. Data will be entered twice and compared for keying errors. These errors will be corrected. Original (unmanipulated) data will be retained by the data manager.

Data reduction will involve a series of steps. The data analyst will retain any intermediate files in PC SAS data sets. Summary information will be provided in charts and tables. A data analysis log will be maintained and will document steps taken in data reduction, any statistical print-outs, and results of any analyses performed.

D.2 Validation and Verification Methods

All data collected will be entered directly onto field data sheets. All data sheets will be validated in the field for accuracy. These data sheets will be placed in a notebook and logged on a daily log sheet. These notebooks will be forwarded to the data manager on a weekly basis. A chain-of-custody sheet will be forwarded with the data logbook. The field crew leader and the data manager will retain copies of the chain-of-custody sheet. The data manager will forward the data sheets to the data entry staff. A chain-of-custody sheet will accompany any and all transfer of raw or electronic data files and the data manager will retain copies of all chain-of-custody sheets. The final verified, computerized data set will be forwarded to the data analysts.

D.3 Reconciliation with Data-Quality Objectives

Data summarizing mean daily, mean monthly and annual nutrient loads, sediment loads and daily mean streamflow will be given to MD DNR for further review and distribution to Chesapeake Bay Resource Managers and researchers.

D.4 Nutrient and Sediment Load Quality Assurance

Estimated nutrient and sediment loads are computed by ESTIMATOR_92 for the calendar year in kg/day (concentration units in water-quality-file are mg/L) with associated standard errors (S.E.) and stand errors of prediction (S.E. PRED.). ESTIMATOR_92 output includes regression diagnostics (Draper and Smith, 1998) section. Visual examination of the output plots, reviewing of errors of prediction, and testing for normality by using the probability plot correlation coefficient (PPCC) test are done on each individual model. The USGS Project Manager is responsible for performing quality control through a technical review by colleague and associate USGSS staff inside and outside the River Input project.

E. References

- **American Public Health Association, 1980**, Standard methods or the examination of water and wastewater, 15th ed.: Washington, D.C., American Water Works Association, Water Pollution Control Federation.
- **Bradu, D., and Mundlak, Y., 1970**. Estimation of lognormal linear models: Journal of the American Statistical Association, 65 (329): p. 198-211.
- Clark, J.W., W. Viessman Jr., M.J. Hanner. 1971. Water Supply and Pollution Control. International Textbook Co., Second Ed.
- **Cohn, T. 1988**, Adjusted maximum likelihood estimation of the moments of lognormal populations from type I censored samples: U.S. Geological Survey Open-File Report 88-350, 34 p.
- Cohn, T.A., Delong, L.L., Gilroy, E.J., Hirsch, R.M., and Wells D., 1989. Estimating constituent loads: Water Resources Research, 25 (5) p. 937-942.
- Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., and Summers, R.M., 1992. The validity of a simple log-linear model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 28, no. 9, p. 2,353-2,364.
- Cohn, T.A., Gilroy, E.J., and Bair, W.G., 1992b. Estimating Fluvial Transport of Trace Constituents Using Regression Model with Data Subject to Censoring, Proceedings of the Joint Statistical Meeting, Boston, Massachusetts, p. 142-151.
- **Colby, B.R., 1955**. The relationship of sediment discharge to streamflow: U.S. Geological Survey Open-File Report, 170 p.
- **Darrell, L.C., Majedi, B.F., Lizarraga, J.S., and Blomquist, J.D., 1999**, Nutrie nt and suspended-sediment concentration, trends, loads, and yields from the nontidal part of the Susquehanna, Potomac, Patuxent and Choptank Rivers, 1985-96: U.S. Geological Survey Water-Resources Investigations report 98-4177, 38 p.
- **Department of Environmental Programs, 1987**, Potomac River water quality 1985, conditions and trends in metropolitan Washington: Washington, D.C., Metropolitan Washington Council of Governments, [variously paged].
- **Draper, N.R. and Smith, H., 1998**, <u>Applied Regression Analysis</u>, 3rd Edition, John Wiley and Sons, Inc., New York, 706 p.
- **Duan, N., 1983**, Smearing estimate: A nonparametric retransformation method. Journal of American. Statistical Association, p. 78(383): 605-610.
- **Duan, N., Manning, W.G., Morris, C.N., and Newhouse, J.P., 1982**, A comparison of alternative models for medical care: Santa Monica, R-2754-HHS. The Rand Corp.

- **Feit, B.A. and Zynjuk, L.D., 1991**, Chesapeake Bay River-Input monitoring quality-assurance quality-control report: U.S. Geological Survey Administrative Report.
- **Ferguson, R.I. 1986.** River loads underestimated by rating curves. Water Resources Research 22(1): p. 74-76.
- **Fishman, M.J., and Friedman, L.C., 1989,** Methods for determination of inorganic substances in water and fluvial sediments, in Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1, 545 p.
- **Friedman, L.C. and Erdmann, D.E., 1982,** Quality assurance practices for the chemical and biological analysis of water and fluvial sediments. In Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A6:181 pp.
- **Gilroy, E.J., Hirsch, R.M., and Cohn, T. 1990**, Mean square error of regression-based constituent transport estimates. Water Resources Research 276(9): p. 2069-2077.
- **Gilroy, E.J., Kirby, W.H., Cohn, T., and Glysson, G.D., 1990**, Discussion of uncertainty in suspended-sediment transport curves by McBean and AI-Nassri. Journal of Hydraulic Engineering 116(1): p. 143-145.
- **Glysson, D.G. and Edwards, T.K., 1988**, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, [variously paged].
- Glysson, D.G., 1987, Sediment transport curves. U.S. Geological Survey Open-File Report 87-218, 47 p.
- **Guy, H.P., 1969**, Laboratory theory and methods for sediment analysis, *in* Techniques of Water-Resources Investigations. U.S. Geological Survey: Book 5, Chapter Cl.
- **Hydrolab Corporation, 1991a**, Surveyor 3, Multiparameter Water Quality Logging System, Operating Manual, Austin, Texas, [variously paged].
- ______, **1991b**, Surveyor 3, H2O Multiparameter Water Quality Transmitter, Operating Manual. Prepared by Hydrolab corporation, Austin, Texas, [variously paged].
- **Koch, R.W., and Smillie, G.M., 1986**, Bias in hydrologic prediction using log-transformed regression models, Water Resources Bulletin 22(5): p. 717-723.
- Lang, D.J. 1982, Water quality of three major tributaries to the Chesapeake Bay, the Susquehanna,Potomac, and James Rivers, January 1979 April, 1981, U.S. Geological Survey Water-ResourcesInvestigations Report 82-32, 64 p.
- **MD Department of the Environment. 1993**, Chesapeake Bay River Input Monitoring Program quality-assurance activities. Chesapeake Bay and Watershed Programs, Baltimore, MD.
- **Miller, C.R. 1951**, Analysis of flow duration, sediment-rating curve method of computing sediment yield: U.S. Bureau of Reclamation Rep. 15 p.

- **Preston, S.D., Biermean, B.J., Jr., and Silliman, S.E., 1989**, An evaluation of methods for the estimation of tributary mass loads. Water Resources Res. 25(6): p. 1379-1389.
- **Thomas, R.B. 1985**, Estimating total suspended-sediment yield with probability sampling. Water Resources Research, 21(g), p. 1381-1385.
- **Thomas, R.B. 1988**, Monitoring baseline suspended sediment in forested basins, The effects of sampling suspended sediment on suspended-sediment rating curves, Hydrologic Science, 33(5), p. 499-514.
- **Sholar, C.J., and Shreve, E.A., 1998**, Quality-Assurance Plan for the Analysis of Fluvial Sediment by the Northeastern Region, Kentucky District Sediment Laboratory: U.S. Geological Survey Open-File Report 98-384, 20 p.
- Skougstad, M.W., M.J. Fishman, M.J., Friedman, L.C., Erdmann, D.E., and Duncan, S.S., 1979, Methods for determinations of inorganic substance in water and fluvial sediments. In U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter Al, 626 p.
- **U.S. Geological Survey, 1983**, Quality assurance plan for water-quality activities of the Mid-Atlantic district, U.S. Geological Survey Administrative Report, 52 p.
- **U.S. Geological Survey. 1992**, Are fertilizers and pesticides in the groundwater? A case study of the Delmarva Peninsula, Delaware, Maryland and Virginia, U.S. Geological Survey Circular 1080, 16 p.
- **Verhoff, F.H., Yaksich, S.M., and Melfi, D.A., 1980**, River nutrient and chemical transport estimation. Journal of Environmental Engineering Division, American Society of Civil Engineering, 106(EE3), p. 591-608.
- Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1987, Methods for the determination of organic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3, 80 p.
- Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., eds, 1998, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, Handbooks for Water-Resources Investigations, [variously paged].
- **Yochum, S.E., 2000**, A revised Load Estimation Procedure for the Susquehanna, Potomac, Patuxent, and Choptank Rivers: U.S. Geological Survey Water Resources Investigation Report 00-4156, 49 p.

Attachment A: Example of Field Data Sheet

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Version 3: 04/2003



U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES



NWIS RECORD NO ___ ___

STATION NO
STATION NAME SAMPLE MEDIUM SAMPLE TYPE TIME DATUM (eg. EST, EDT, UTC)
PROJECT NO PROJ NAME SAMPLE PURPOSE (71999) PURPOSE OF SITE VISIT (50280)
SAMPLING TEAM
START TIME GAGE HT TIME GHT TIME GHT GHT GHT GHT
OC SAMPLE COLLECTED? EQUIP BLANK FIELD BLANK SPLIT CONCURRENT SEQUENTIAL SPIKE TRIP BLANK OTHER NWIS RECORD NOS.
LABORATORY INFORMATION SAMPLES COLLECTED: NUTRIENTSMAJOR IONSTRACE ELEMENTS: FILTEREDUNFILTEREDMERCURYVOCRADON TPC(VOL FILTEREDmL) TPC(VOL FILTEREDmL) PIC(VOL FILTEREDmL) DOCORGANICS: FILTEREDUNFILTERED SOTOPESMICROBIOLOGYCHLOROPHYLLBODCODALGAEINVERTEBRATESFISHBED SED SUSP. SEDconc. s/f sze RADIOCHEMICALS: FILTEREDUNFILTEREDOTHEROTHER LABORATORY SCHEDULES:
FIELDMEASUREMENTS
GAGE HT (00065) ft COND (00095)µS/cm@25 °C CARBONATE (00452)mg/L
O, INST. (00061)Cfs meas. Rating est. Temp, Air (00020)°C Hydroxide (71834)mg/L
DIS. OXYGEN (00300)mg/L
BAROMETRIC PRES. (00025) mm Hg
DO SAT. (00301) % ALKALINITY ()mg.L TOTAL COLFORM (31501) col/100 mL
eH (00090)mvolts ANC ()mg/L OTHER:
pH (00400)units Bicarbonate (00453)mg/L Other:
SAMPLING INFORMATION
Sampler Type (84164) Sampler ID Sample Compositor/Splitter: PLASTIC TEFLON CHURN CONE OTHER
Sampler Bottle/Bag Material: PLASTIC TEFLON OTHER Nozzle Material: PLASTIC TEFLON OTHER Nozzle Size: 3/16" 1/4" 5/16"
Stream Width: ft mi Lef Bank Right Bank Mean Depth: ft lce Cover % Ave. lce Thickness in.
Sampling Points:
Sampling Location: WADING CABLEWAY BOAT BRIDGE UPSTREAM DOWNSTREAM SIDE OF BRIDGE
Sampling Site: POOL RIFFLE OPEN CHANNEL BRAIDED BACKWATER BOTTOM: BEDROCK ROCK COBBLE GRAVEL SAND SILT CONCRETE OTHER
Stream Color: Brown Green blue gray clear other Stream Mixing: well-mixed stratified poorly-mixed unknown other
Weather: SKY- CLEAR PARTLY CLOUDY CLOUDY PRECIP- LIGHT MEDIUM HEAVY SNOW RAIN MIST WIND- CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED
Temp- very cold warm hot comments Sampling Method (82398): ew [10] edi [20] single vertical [30] multivertical [40] other Stage: stable, normal stable, high rising falling peak OBSERVATIONS:
COMPILED BY:

ı		
STN NO		

						METEF	R CALIBRAT	IONS			
TEMPERA	ATURE Meter	MAKE/MODEL _			S/N _		Ther	mister S/N		_ Thermome	eter ID
Lab Teste	d against NIST	Thermomete	r/Thermister?	N	Y Dε	ate:	JJ		±	°C	
Measurem	ent Location:	CONE SPLITI	ΓER CHURN	SPLITTER	SING	LE POINT AT	·ft r	DEEP VERTIC	CAL AVG. OF _	POINTS	
FIELD RE	ADING # 1	# 2	#3_		_ # 4		# 5	MEDIAN	N:	°C REN	MARK QUALIFIER
pH Mete	rmake/model _			S/N			Electron	de No		Type: GEL	LIQUID OTHER
Sample:	FILTERED UNFIL	LTERED (ONE SPLITTER	CHURN	N SPLITTEF	R SINGI	LE POINT AT _	FT DEEP	VERTICAL	L AVG. OF	POINTS
pH BUFFER	BUFFER TEMP	THEO- RETICAL pH FROM TABLE		pH : AFTER ADJ.	SLOPE		BUFFER LOT NO.	BUFFER EXPIR A- TION DATE	COMME	NTS	TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED?
pH 7	+					 					CALIBRATION COMMENTS:
pH 7											
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pH											
pH											
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CHECK			.								
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FIELD RE	ADING # 1	#2		# 3	#	# 4	#5	USE:	:	_ UNITS REM	MARK QUALIFIER
SPECIFIC	CONDUCTAN	NCE Meter M.	AKE/MODEL				S/N		_ Sensor Ty	ype: DIP C	CUP FLOW-THRU OTHER
Sample:	CONE SPLITTER	₹ CHURN S	PLITTER S	INGLE POINT	T AT	ft deep	, VERTICA	AL AVG. OF	_ POINTS	Tempera	ature compensation:
STD VALUE	STD TEMP	SC BEFORE ADJ.	SC AFTER ADJ.	STD LOT NO		EXPIRATION DATE	ON	COMMENT	-S	AUTO	O UAL CORR. FACTOR =
	 				†						
	<u></u>										
FIELD RE	ADING # 1	#2	<u> </u>	#3		¥ 4	# 5	MEDIA	AN:	_mS/cm RE	MARK QUALIFIER
DISSOLV	ED OXYGEN	Meter MAKE/M	ODEL			S/N _		Pi	robe No		
Sample:	SINGLE POINT	AT f	ft deep ve	ERTICAL AVO	3. OF	POINTS	BOD BOT	TLE OTHER_		St	tirrer Used? Y N
Air Calibra	tion Chamber in	n Water	Air-Saturated	Water	_ Air Ca	libration Ch	amber in Air	Winkler T	itration (Other	
Battery Ch	eck: REDLINE_	RANGE	-	THEF	RMISTEF	R Check?	Y N _		Zero	o DO Check:	Y N Solution Date
WATER TEMP °C	BAROMETRIC PRESSURE mm Hg			BEFO	ORE	DO AFTER ADJ.		ter Reading ne Changed?		,	mg/L / Time:
		1a			<u>- </u>	7100.	•	Ü			Time:
	L	<u> </u>	<u> </u>	<u> </u>			-				
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Attachment B: Example of Quarterly Report to Maryland Department of Natural Resources

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SAMPLE

Chesapeake Bay River Input Monitoring Program: Quarterly Progress Report

MARYLAND

Project Number: MD 4424-9B201

Monitoring Sites:

•	(01578310)	Susquehanna River at Conowingo Dam, Maryland
•	(01646580)	Potomac River at Chain Bridge, District of Colombia
	(0.4 = 0.4.4.4.0)	D D

(01594440) Patuxent River near Bowie, Maryland
 (01491000) Choptank River near Greensboro, Maryland

Report Period: January 1, 2003 - March 31, 2003

Funding: Maryland Department of Natural Resources (Md DNR) and U.S. Geological Survey (USGS)

Start Date: July 1985

Completion Date: continuous

Project Personnel: USGS Chief: Mick Senus; USGS Lead Technician: Dave Brower and additional assistance from various other USGS district personnel. Comparative sampling at Chain Bridge by Occoquan Watershed Monitoring Laboratory (OWML, Manassas, Va.) is performed by Harry Post (chief) and Phil Spellerberg (technician) and managed by Christine Howard of Metropolitan Washington Council of Governments (MWCOG).

Project Objectives:

- Determine the ambient concentration of nutrient and suspended sediment water-quality samples
 collected over a range in flow conditions near the point of tidal influence of four major Maryland
 tributaries to the Chesapeake Bay: the Susquehanna, Potomac, Patuxent and Choptank Rivers.
- Estimate monthly, and annual loading of nutrients and suspended sediment entering the Chesapeake Bay from the non-tidal portions of the Susquehanna, Potomac, Patuxent and Choptank Rivers.
- Identify trends in constituent concentration data at the four tributary stations.

This Quarter's Sampling Events:

		Sample Type				
	Routine	QA/QC				
Susquehanna @ Conowingo	3	5	2			
Potomac @ Chain Bridge	3	3	1			
Patuxent nr. Bowie	3	4	1			
Choptank nr. Greensboro	3	3	1			

SAMPLE

SAMPLE

This Quarter's Activities:

- Maryland RIM will use DH-95 (D-95) for flow greater than 2 feet/second at Patuxent and Choptank monitoring stations. This does not apply to Chain Bridge at Potomac due to safety concerns on the downstream side of the bridge and lack of room for bridge-board and reel. This does not apply to Conowingo at Susquehanna due to unique water conditions (caused by dam turbine-outflow(s)) making an iso-kinetic sampler such at the D-95 or DH-95 unfit for proper function and use (i.e ater too turbulent).
- This quarter RIM stopped sampling for NAWQA at its Routine sampling collections at Chain Bridge (Potomac R.). Beginning in January 2003, separate sampling runs for NAWQA and RIM at Potomac R. at Chain Br. (NAWQA 1st week/mo, RIM 3rd week/mo). Note: RIM had been sampling for both its project and Potomac-NAWQA at the same time by one technician (D. Brower). This change has occurred because of disparities in analytes collected and differences in sample collection methods between RIM and NAWQA.
- This quarter RIM began sampling <u>storms</u> at Chain Bridge (Potomac R.) and conduct comparative study in collection method with MWCOG for Calendar Year 2003. Dave Brower has coordinated with Harry Post to sample routinely on same day fixed frequency for baseflow and weather dependent for stormflow.
- This quarter Pennsylvania-NAWQA no longer sampled at Conowingo (Susquehanna). RIM will continue its routine and storm flow sampling. PA-NAWQA will pay for additional analysetes, labor, and shipping charges. No impact to RIM except drop in baseflow sampling events (12 instead of 24).
- WQ Data from Christine Howard (MWCOG) for calendar year (CY) 2002 was sent and received by the USGS in order to estimate loads.
- Load estimation for CY 1994-2002 began this quarter.
 - Beginning January 1, 2003- Changes in RIM sampling program as a result of meeting with MdDNR and USGS on December 4th, 2002 and Non-Tidal Workgroup meeting on December 17th, 2002:
 - 1. Particulate Inorganic Phosphorus (PIP) and Particulate Phosphorus (PP)
 - 2. Dissolved Organic Carbon (DOC), Particulate Inorganic Carbon (PIC) and Particulate Carbon (PC)
 - 3. Particulate Nitrogen (PN)
 - 4. Total Dissolved-Nitrogen (TDN) and Total Dissolved-Phosphorus (TDP) by the **alkaline persulfate** digestion method.
 - 5. sand/silt/clay spilts (1 storm/quarter)
 - 6. Volatile Suspended Solids (VSS)
 - 7. BOD (low priority)
 - 8. particulate NH4 (lowest priority)
 - MdDNR will cover cost of PP and PIP analyses at CBL.
 - To satisfy the Chesapeake Bay Watershed Model (WSM), MdRIM will keep doing TOC for 1 year for comparison study against DOC, PIC, and PC.

SAMPLE